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PART XVIII

## VAPORIZATION OF COMPOUNDS AND ALLOYS OF HIGH TEMPERATURE

PART XVIII. MASS SPECTROMETRIC AND KNUDSEN CELL VAPORIZATION  
STUDIES OF II<sub>b</sub> - VI<sub>b</sub> COMPOUNDS

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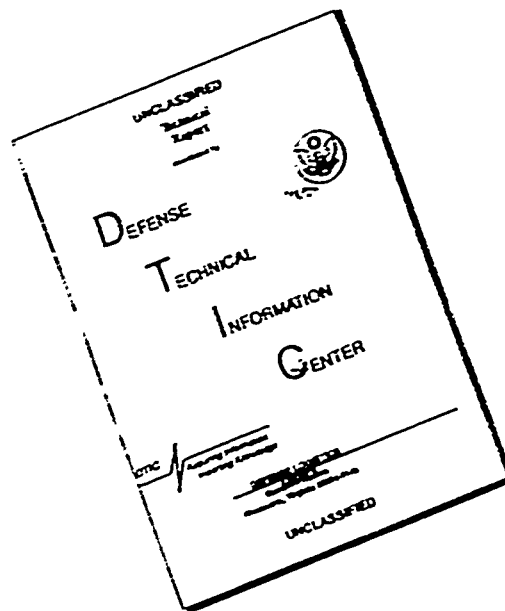
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## FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-Graphitic." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

Thanks are due to Mr. R. Colin for performing some mass spectrometric experiments and for many valuable discussions, to Miss A. Steinchen and M. Stoefs for performing many Knudsen experiments.

# ABSTRACT

The vaporization process of the compounds of Zn, Cd, Hg with S, Se, Te has been studied by mass spectrometry. The heat of decomposition of all these compounds to  $M(g) + 1/2 X_2(g)$  has been measured by mass loss Knudsen technique. The data are compared to literature data. Heats of atomization of these compounds are compared to isosteric compounds and upper limits for the dissociation energies of the gaseous molecules are given.

This technical documentary report has been reviewed and is approved.



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## SUMMARY

The vaporization process of the nine compounds of Zn, Cd and Hg with S, Se and Te has been investigated by mass spectrometry. The typical process is the decomposition into gaseous metal atoms and diatomic group VI<sub>b</sub> molecules. Small amounts of polymeric species of sulfur were observed in the vapor above HgS and considerable amounts of polymeric selenium molecules above HgSe ; HgTe yields Hg(gas) and solid Te. -No gaseous II<sub>b</sub>-VI<sub>b</sub> molecules were observed : their concentration lies below 1 part in 10<sup>3</sup> to 10<sup>5</sup>. Estimates of dissociation energies are made and the possibility of observing these molecules is discussed. - Decomposition pressures of all nine compounds were measured by the Knudsen method and corresponding enthalpy and entropy data deduced and compared to literature data. - The heat of vaporization of lead has been remeasured. The heats of atomization of the II<sub>b</sub>-VI<sub>b</sub> compounds are compared to those of isosteric compounds and elements and the trends are discussed.

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Spandau<sup>(17)</sup> □, Hsiao<sup>(16)</sup> Δ, Neuhaus<sup>(14)</sup> ⊕, this paper ●  
Least squares second law value  $\Delta H_{1075}^0 = 177$  or  $\Delta H_{298}^0 = 188.9$  kcal,  
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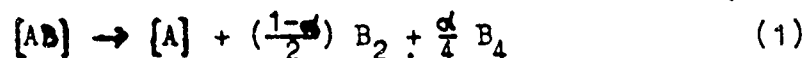
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## INTRODUCTION

In the last decade vaporization studies, using mainly mass spectrometric techniques, have demonstrated the complexity of numerous inorganic vapors<sup>(1)(2)</sup>. The vapors of group IV elements, for instance, contain polymeric species<sup>(3)</sup> and it was expected that isoelectronic or isosteric<sup>(\*)</sup> III<sub>b</sub>-V<sub>b</sub> and II<sub>b</sub>-VI<sub>b</sub><sup>(\*\*)</sup> compounds form gaseous and perhaps polymeric molecules especially as some corresponding I<sub>b</sub>-VII<sub>b</sub> compounds are known to form trimers in the gas phase<sup>(4)</sup>. Also the IV-VI compounds, isosteric to group V elements form polymeric molecules<sup>(5)</sup>. Previous mass spectrometric studies<sup>(6,7)</sup> have shown however that III<sub>b</sub>-V<sub>b</sub> compounds vaporize mainly according to



where A is a group III<sub>b</sub> and B a group V<sub>b</sub> element. (Here and throughout this paper square brackets  $[ ]$  are used for the condensed phase, without distinction between solid and liquid state). The only gaseous molecules of this group as yet described are InSb and InSb<sub>2</sub><sup>(8)</sup>. Mass spectrometric work from

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(\*) Isoelectronic molecules contain the same number of electrons e.g. Ge<sub>2</sub>, GaAs, ZnSe; isosteric molecules contain the same number of outer electrons even though the total number of electrons is different e.g. Ge<sub>2</sub>, AlSb, InP, CdS, MgTe.

(\*\*) The classification in subgroups a and b as given by Pauling (The Nature of the Chemical Bond, 2d ed. Cornell University Press 1960, p.54) is used here.

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this laboratory<sup>(6)</sup> has shown that also II (Me)-VI (X) compounds decompose on vaporization. The general process is however



as further confirmed by recent data for ZnS, CdS and HgS<sup>(9)</sup>.

A survey of existing data on vaporization of these compounds obtained by conventional manometric, transport or Knudsen method leads to two conclusions :

a) some data<sup>(10-14)</sup> are presented assuming eqn.(2), others are based on the assumption of molecular vaporization<sup>(15-17)</sup>



the justification of the choice in the earlier literature being rather incomplete as will be discussed below.

b) the data recalculated according to the correct vaporization process show in quite a number of cases considerable discrepancies; finally most papers treat the vaporization of a small number of compounds or even of a single compound.

We have therefore studied the vaporization of all nine compounds of Zn, Cd and Hg with S, Se and Te and have used mass spectrometric analysis of the vapors and have confirmed the general applicability of the vaporization eqn.(2). In no case could eqn.(3) be observed, therefore only an upper limit of the dissociation energies of gaseous MeX compounds can be given. Next the decomposition pressures of all nine compounds have been measured by the conventional Knudsen technique without mass separation and the corresponding thermodynamic properties have

been obtained. They will be presented and discussed in a comprehensive way.

Finally, the partial pressure at a given temperature of  $B_2$ ,  $B_4$ ,  $X_2$  given by the equilibria (1) and (2) being lower than the vapor pressure in equilibrium with condensed B or X new data could be obtained on equilibria with species  $B_n$  or  $X_n$  (6,18).

## EXPERIMENTAL.

### 1. Mass Spectrometric Technique.

The main features of the 60° 20 cm radius of curvature mass spectrometer and of the experimental procedure have been described previously<sup>(6)</sup>. Vaporization was performed from small graphite crucibles in a molybdenum furnace heated by a tungsten spiral. The crucible was located at about 10 mm from the ionizing electron beam. Some experiments were performed using quartz Knudsen cells and a secondary electron multiplier. Special care was taken in locating in the furnace the 0.1 to 0.05 mm diameter Pt-Pt/10% Rh - thermocouple wires insulated with tiny quartz tubes, in such a way as to minimize errors due to overheating from the tungsten spiral or heat loss through the thermocouple leads. Frequent temperature checks were performed by comparison with a Leeds and Northrup disappearing filament optical pyrometer in the temperature range above 1000°K and by measuring in situ the melting point of Se (490°) and Ag (1234°K),

using the method of Johnson et al<sup>(19)</sup>.

Samples of one to several tenths of a gr. were loaded in the crucible or in the Knudsen cell. The mass spectrometer was evacuated and the crucible heated slowly maintaining the background pressure at or below  $5 \cdot 10^{-7}$  mmHg. The mass spectrum was then scanned and ionic species originating from the vaporizing substance as well as possible impurities identified at different temperatures. In a number of runs with ZnS, accurately weighed amounts were completely vaporized in order to measure the sensitivity of the mass spectrometer and the absolute value of the decomposition pressure<sup>(20)</sup>.

## 2. Knudsen Technique.

Quartz Knudsen cells of about 1 cm<sup>3</sup> volume were used. The effusion area was measured within about 10 % with a microscope and on magnified photographs. The wall thickness was measured on several Knudsen cells which were broken for this purpose after use. The areas and corrections for wall thickness are discussed below. The cells were inserted in a stainless steel oven, heated by radiation from a W ribbon and provided with radiation shields. Temperature measurements were performed as in the mass spectrometer technique. After about five runs new thermocouple wires were inserted in order to avoid use of wires deteriorated by the vapors. The shielded oven was placed in a stainless steel vacuum housing pumped through

a liquid air trap by a 100 liter  $\text{sec}^{-1}$  Hg vapor diffusion pump. Opposite the effusion orifice a liquid air trap served for condensing the effusing vapor. The background pressure was kept below  $10^{-5}$  mmHg, frequently below  $10^{-6}$  mm.

Samples of 1 to 2 grs of crushed crystals were weighed to about 0.01 mg; after obtaining the adequate residual pressure, the oven was heated rapidly to the desired temperature maintained within 1 to 2° at constant temperature for the required time and cooled rapidly by cutting the power supply and the residue weighed again. Heating and cooling times were controlled ; from total weight loss a "preliminary graph"  $\log p$  vs.  $1/T$  was obtained, where T is the constant temperature of the experiment. This permits one to calculate the amount vaporized during the heating and cooling period and to obtain the weight loss at the constant temperature and a "correction" for the vapor pressure value. This correction was not significant however as checked for every experiment, and shown as an example in table 5 (col.(a) and (b)).

### 3. Materials.

High purity crystals kindly supplied by  
Dr. Van Kaekenberghe (E.R.A., Brussels) (CdS CdSe)  
Dr. P. Newman (Philips Eindhoven) (ZnS, ZnTe), Dr. W. Lawson  
(Royal Radar Institute) (CdTe HgTe) and commercial samples  
(ZnS, Fluka ; H<sub>2</sub>S Hopkins and Williams) purified by sublima-

tion under high vacuum were used. The purity was checked by mass spectrometric analysis.

#### CALCULATIONS.

Knudsen evaporation permits one to calculate the pressure of a vaporizing species  $i$

$$p_i = Z_i (2\pi k T m_i)^{1/2} / s t \quad (4)$$

where  $Z_i$  is the number of molecules of species  $i$  effusing in time  $t$ ,  $m_i$  the mass of these molecules and  $s$  the "effective" orifice area ; the other symbols have their usual meaning. For the simple vaporization process given as no. 1 in Table 1, the corresponding formula for weight loss  $G_i$  is given; the pressure in atmospheres is then obtained from

$$p_i = 2.256 \times 10^{-2} G_i (T/M_i)^{1/2} / t.s \quad (5)$$

$G_i$  in grs,  $M_i$  in a.m.u.,  $t$  in sec and  $s$  in  $\text{cm}^2$ . Throughout this paper pressures will be given in atmospheres.

For congruent vaporization according to no. 2 and 3 in Table 1

$$2Z(X_2) + Z(X) = Z(\text{Me}) \quad (6)$$

and

$$G = G(\text{Me}) + G(X_2) + G(X) = Z(\text{Me}).m(\text{MeX}). \quad (7)$$

One obtains thus the equations for  $p(\text{Me})$ ,  $p(X_2)$ ,  $p(X)$  and  $K$  given in Table 1.



Heats of reaction were calculated using the third law method

$$-RT \ln \kappa = \Delta H_{298}^0 + T \Delta \left( \frac{G^0 - H_{298}^0}{T} \right) \quad (8)$$

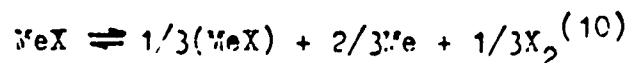
in cases in which free energy functions,  $(G^0 - H_{298}^0)/T$ , were available and a comparison was made with the second law value

$$H_T^0 = -R \frac{d \ln \kappa}{d (1/T)} \quad (9)$$

The latter values were also used when data on entropies seemed insufficient and entropies were then estimated by inserting  $\Delta^0$  in eqn.(8).

For minor species it is of interest to introduce a free energy change, the chemical stability<sup>(21)</sup>, a measure of the relative concentration of these species compared to a major species. Two cases are of interest here

a) the chemical stability of  $MeX$  molecules which results from combining eqn.(2) and (3)

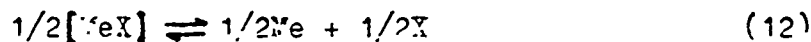


is given by<sup>(21b)</sup>

$$\begin{aligned} & -RT \ln p(X_2)/p(MeX) \\ & = \{D_0^0(MeX) - H_0^0(at.MeX)\} - 1/3 \{D_0^0(X_2) - H_0^0(at.MeX)\} \\ & + T \Delta \left( \frac{G_T^0 - H_0^0}{T} \right) + 1/3 RT \ln \{M(Me)/M(X_2)\} \end{aligned} \quad (11)$$

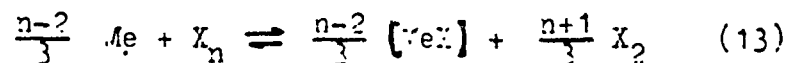
The last term results from the Knudsen equation and the stoichiometry of eqn.(2),  $M( )$  are the masses of species in ( ); the difference of free energy function  $\Delta(G_T^0 - H_0^0/T)$  refers to the stoichiometry of eqn.(10);  $D$  is the dissociation energy; the

Heat of atomization  $\Delta H(\text{at.MeX})$  corresponds to



The free energy functions are known or can be estimated as discussed below;  $D_0^0(\text{X}_2)$  have been measured previously<sup>(18)</sup> and  $\Delta H_0^0[\text{at.MeX}]$  are obtained from the heats of decomposition measured here and corresponding to eqn.(2).

b) the chemical stability of different species of group VI<sub>b</sub> elements  $\text{X}_n$ , with  $n=1, 3 \dots$ , results from the equilibrium



and the corresponding free energy change (for  $p(\text{X}_n) \ll p(\text{X}_2)$ )

$$\begin{aligned} & -RT \ln p(\text{X}_2) p / (X_n) \\ & = \{ \Delta H_0^0(\text{at.X}_n) - (n-1) \Delta H_0^0(\text{at.MeX}) \} - \frac{n+1}{3} \{ D_0^0(\text{X}_2) - H_0^0(\text{at.MeX}) \} \\ & + T \Delta \left\{ (G_T^0 - H_0^0) / T \right\} - \frac{n-2}{3} RT \ln \{ 4M(\text{Me}) / M(\text{X}_2) \}^{1/2} \quad (14) \end{aligned}$$

The symbols have the same significance as in eqn.(11) and  $\Delta H_0^0(\text{at.X}_n)$  corresponds to



## RESULTS.

### 1. Mode of evaporation of the II<sub>b</sub>-VI<sub>b</sub> compounds.

For all Zn and Cd compounds ions  $\text{Me}^+$ ,  $\text{X}_2^+$  and  $\text{X}^+$  were observed, the intensity ratios being constant at different temperatures and during complete evaporation of the samples. The

observed intensity of  $X^+$  is readily explained as fragmentation of  $X_2$  by electron impact.

The ion intensities ( $I^+$ ) of  $X_2^+$  and  $Me^+$  are related to partial pressures ( $p_i$ ) and ionization cross sections ( $\sigma_i$ ) by

$$I^+ = kp_i\sigma_i \quad (15a)$$

$k$  is a constant depending on the geometry of the vaporization cell with respect to the mass spectrometer as well as on the properties of this instrument<sup>(1,6)</sup> but independent of mass.

Then the stoichiometry (eqn.2) and the Knudsen equation (eqn.4) yield

$$\sigma(X_2)/\sigma(Me) = \left(2I^+(X_2)/I^+(Me)\right) \left(u(Me)/u(X_2)\right)^{1/2} \quad (15b)$$

$\sigma(X_2)/\sigma(Me)$  values calculated from ratios of ion intensities, or integrated ion intensities in the course of complete vaporization are given in table 2. The values given by Otvos and Stevenson<sup>(22)</sup> for ionization cross sections of atoms permits one to calculate ratios of ionization cross sections of  $X_2$  molecules to  $X$  atoms. The results given in column 4, Table 2, with an estimated error of about 0.1 or 0.2 are well in line with several recent determinations of ratios of ionization cross sections of about 1.5 <sup>for</sup> homonuclear diatomic molecules compared to atoms<sup>(23,18b)</sup>.

All these data confirm vaporization eqn.(2) as well as the fact that all these compounds have<sup>(24)</sup>, within the experimental accuracy of a few per cent of the present measurements,

an exact stoichiometric composition.

For HgS about 2-3%,  $S_6^+$  and minor contributions of ions up to  $S_7^+$  were observed. Eqn.(14) permits one, using thermodynamic data quoted below and  $S_{500}^0(S_6) \approx 100$  e.u., to calculate the heat of atomization  $\Delta H_{500}^0(\text{at. } S_6) = 365$  kcal ; no correction was applied for ratios of ionization cross sections. For the reaction



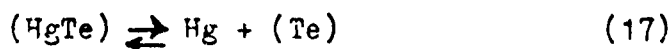
$\Delta H_{500}^0 = 62.9$  kcal is found. It is estimated that errors ; including the uncertainty in ionization cross sections, amount to about 3-4 kcal. The agreement with the mass spectrometric results of Berkowitz and Marquart who obtain 63.3 kcal<sup>(3)</sup> and with the value of 63.7 kcal obtained from total pressure measurements on sulfur vapor by Braune, Peter and Nevelling<sup>(25)</sup> is satisfactory.

A typical mass spectrum of the vapor from HgSe is given in Table 3. The complexity of the vapor does not permit one in this case to deduce enthalpy values corresponding to a definite process from mass loss Knudsen measurements. From the ratios of  $Se_6^+/Se_2^+$  ion intensities the enthalpy corresponding to eqn.(2) can be calculated; fragmentation by electron impact was neglected and an equation similar to (14) was used. The heat of reaction corresponding to (16) and the necessary entropy data are known<sup>(26)(\*)</sup>. The result is  $\Delta H_{500}^0 = 45$  kcal per mole for

(\*) The entropy of  $[HgSe]$  solid at 500°K was estimated 28 e.u. by analogy with  $[HgS]$ .

eqn.(2) and the heat of formation from the elements  $\Delta H_{f298}^0(\text{HgSe}) = -14$  kcal per mole. Table 3 shows also that, if stoichiometry is exact, the ionization cross sections from  $\text{Se}_2$  to  $\text{Se}_6$  vary scarcely more than by a factor of two; a more accurate estimate is not possible with present data.

(HgTe) vaporizes according to



A careful search was made in each case for ions which could originate from gaseous  $\text{MeX}$  molecules, but in no case could any evidence for these be found. Therefore in eqn.(11) only an upper limit of  $p(\text{X}_2)/p(\text{MeX})$  can be inserted and an upper limit of  $D(\text{MeX})$  calculated. The results are given in table 4. For Zn, Cd and Hg, sulfides a recent investigation<sup>(7)</sup> has succeeded in shifting the limit  $p(\text{X}_2)/p(\text{MeX})$  to above  $10^5$  and to detect at this sensitivity limit  $\text{S}_3^+$  and  $\text{S}_4^+$  in the vapor above (ZnS) and (CdS) as well as the species observed by us above (HgS).

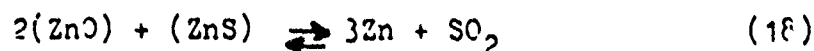
## 2. Decomposition pressures by Knudsen technique.

a) In order to test the performance of the Knudsen technique a set of experiments of the vaporization of lead were performed (Table 5). It appears that the correction for temperature rise and fall is small; the Clausius factor is a maximum estimate, therefore taking the average  $\Delta H_{298.15}^0 = -46.7$  kcal/g

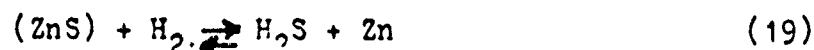
atom may result in a negligible error due to this parameter. A possible systematic error in temperature measurements ( $\delta T = 3^\circ$ ), in the surface area (10%) as well as the scatter of the experimental results leads to an estimated uncertainty of  $\pm 0.5$  kcal. The second law value,  $\Delta H_{298}^0 = -45.2 \pm 0.3$  kcal, yields  $\Delta H_{298}^0 = -47.7$  in satisfactory agreement with the above result. The systematic error is however as large as  $2 \delta T / (T_1 - T_2) = 5\%$ . The third law value is in excellent agreement with the value  $\Delta H_{298}^0 = -46.80$  kcal chosen by Stull and Sinke<sup>(26)</sup> and with the recent result of Aldred<sup>(23)</sup>.

b) The results on the vaporization of the three sulfides as treated by the third law method are given in tables 6, 7 and 8. In figs. 1 and 2 and in Table 9 the second law treatment of our results is included and all our data compared to literature.

In the figs. 1 and 2 and in table 9 effusion data (12, 14, 15, 16) and apparent vapor pressures<sup>(17)</sup> were converted to decomposition equilibrium constants corresponding to eqn. (2). Also the equilibrium constants of reactions



studied by Okunev and Popovkina<sup>(38)</sup> and



studied by Richards (I)<sup>(13)</sup> were converted to  $K = p^2(\text{Zn}) \cdot p(\text{S}_2)$ .

Richards has also investigated the decomposition pressure of ZnS by the transport method in a stream of  $N_2$ (II) and  $N_2+S_2$ (III) giving the correct equilibrium constant.

For ZnS the vapor pressure measurements extend from about 1000 to 1600°K. Freeman<sup>(29)</sup> chooses a  $\Delta H_{f,298} = -49.2 \pm 0.5$  kcal using the same data as here; this small difference may be due to a somewhat different choice of free energy functions.

Table 6 shows a systematic difference of 0.7 kcal between experiments n°1 to 8 and 9 to 13. A combined error of 5% in measuring the area of the two orifices explains the main difference.

Disagreeing results are those of Okunev, Averbukh et al.<sup>(33)</sup> and of Neuhaus and Retting<sup>(14)</sup> whose immediate purpose was not the determination of the decomposition pressure or vapor pressure of ZnS. Those of Hsiao and Schlechten<sup>(15)</sup> disagree with accepted values by several powers of 10 also for many other substances even though the slope agrees reasonably with our data<sup>(6d)</sup>.

For CdS, Spandau and Klanberg's<sup>(17)</sup> data recalculated and ours fall on a very nice straight line, which has permitted us to perform a least squares 2nd law treatment from 850 to 1450°K. The conversion to 298°K was made using  $T_p$  from Russel<sup>(39,40)</sup>.

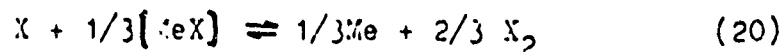
Again the decomposition pressures given by Neuhaus and

Retting<sup>(14)</sup> are high, those of Hsiao and Schlechten<sup>(16)</sup> low. Recalculation of the CdS + H<sub>2</sub> equilibrium measured by Britzke and Kapustinskii<sup>(41)</sup> leads to an equilibrium constant low by many powers of ten.

For red HgS, the difference between the two sets of data taken with an orifice area varying by about a factor of 15 (table 8) is larger than in the case of ZnS and CdS. Nevertheless it scarcely lies outside experimental uncertainty.

c) The results for HgSe have been discussed above (Results 1), the other selenides and tellurides were treated by the second law method; they are presented in figs.3-7 and table 10 and compared to literature data.

Specific heats have been estimated in all cases using Zubischewski's procedure (l.c.<sup>(27)</sup>, page 183) i.e. a linear increase from the value at 298°K to the first transition point. For the tellurides of Zn and Cd the Te<sub>2</sub> ⇌ 2Te equilibrium was checked ; using eqn.(13) and (14) with n=1 one finds



and

$$\begin{aligned} -RT \ln p(X_2)/P(X) = & 2/3 \{ \Delta H_0^0(\text{at. TeX}) - \Delta_0^0(X_2) \} \\ & + T \Delta \{ (3T^0 - H_0^0)/T \} + 1/3 RT \ln \{ 4M(\text{Te})/M(X_2) \}^{1/2} \end{aligned} \quad (21)$$

For CdTe the dissociation of Te<sub>2</sub> increases with temperature; it is however negligible in the temperature range investigated, whereas for ZnTe about 4% of Te<sub>2</sub> is dissociated independently



of temperature: the correction using eqn.no.3 of table 1 was applied. From figs. 3-7 and table 10 it appears that our data agree well with those of Korneeva<sup>(42)</sup>, McAteer<sup>(45)</sup> and Lorenz<sup>(46)</sup>; comparing the 9 compounds the results of Somorjai<sup>(43)</sup> seem to lie quite out of line. For ZnSe Korneeva's data and for ZnSe and CdSe those of Wösten disagree if a second law treatment is used; a third law treatment with the entropy obtained from our results reduces the disagreement considerably.

HgTe is treated according to 1.b) table 1.

## DISCUSSION.

1. The primary object<sup>(3d,e)</sup> of this research was to study  $S_2$ ,  $Se_2$  and  $Te_2$  vapor at the saturation pressure above II-VI compounds which is well below that above the group VI elements, and to observe thus the dissociation equilibria  $X_2 \rightleftharpoons 2X$ . In order to accomplish this even in the case of selenides and tellurides<sup>(18b,c)</sup> it was necessary to superheat the vapor and to use the so-called double oven technique. For the study of the  $S_2 \rightleftharpoons 2S$  equilibrium even this technique was insufficient and the much more refractory sulfides of calcium, strontium and barium had to be used<sup>(18a)</sup>. As to the complex equilibria of polymeric group VI species (eqn.15) some confirmation of earlier literature data<sup>(26)</sup> have been obtained by the mass spectrometric method (see also ref.9), which appears to be more direct but not quite easy to handle in such cases.

2. The mass spectrometric investigation of the vaporization of the nine compounds of Zn, Cd, Hg with S, Se and Te has permitted us to settle the equilibrium vaporization process of these compounds and thus to calculate heats of decomposition according to eqn.2. In all cases the concentration of gaseous  $MeX$  molecules is below our detection limit ( $10^{-3}$  -  $10^{-5}$ ). In some earlier work, the correct process had been assumed because measured pressures and those calculated from eqn.2 and

thermochemical data were found to be in agreement<sup>(12-14)</sup>; such proofs are however only valid if extremely accurate data are available and even in that case their sensitivity to the presence of minor species is very bad. The situation is somewhat better in transport experiments (e.g. ref.13). The spectroscopic data<sup>(47)</sup> must be considered as doubtful.

From table 4, it appears that even molecules with relatively high dissociation energy may have a low chemical stability, i.e. relative concentration. Further their relative concentration increases with increasing temperature has been emphasized in recent years in a number of high temperature studies<sup>(2,4,6,18,21)</sup>. It is interesting then to make an estimate using eqn.11, of conditions for observing these molecules. It has been shown recently<sup>(21)</sup> that, although dissociation energies of various diatomic molecules differ considerably, the variation of the ratio  $\alpha = \Delta H(\text{at. AP})/D(\text{AP})$  is fairly small, especially in selected, chosen groups of binary compounds. From table 4 and 11 one finds the highest value  $\alpha > 1.7$  for ZnTe; for InSb,  $\alpha = 1.3$  and for Sn,  $\alpha = 1.5$  have been found<sup>(21)</sup>. Assuming that for all compounds investigated here  $\alpha \approx 2$ , an increase of 2-300° in temperature and of one or two powers of ten in pressure should permit one to observe ZnTe and CdTe; for sulfides and selenides the temperature range of 1500-2000°K and pressures near one

atmosphere would be necessary. Experimental developments are made now to test the case of the above mentioned two molecules.

3. Table 3 shows, that the third law treatment of experimental data has permitted one to obtain a very satisfactory agreement on heats of formation of sulfides. It seems that the proposed values are reliable within about 0.5 kcal. The comparison of 2nd and 3rd law values in Table 3 as well as for the case of the vaporization of lead shows that 2nd law values may be in error by about  $\pm 2$  kcal: this appears also in table 10, which shows even some stronger disagreements. It is however estimated that the proposed values are reliable within  $\pm 2$  kcal.

4. Necessarily the entropy values obtained from vaporization data treated by the second law (table 10) are uncertain within about 2 e.u. A monotonic increase from [ZnS] to [HgTe] is expected as well from an ionic model<sup>(48)</sup> as from a "covalent" model of the solids (comparison with isosteric group IV elements). For the light II<sub>b</sub>-VI<sub>b</sub> compounds, the measured entropy values lie between those calculated by the two models; for [CdTe], [HgSe] and [HgTe] the observed value is well below the calculated value.

5. The question may arise whether some inconsistencies in decomposition pressure data are due to a low vaporization coefficient as suggested for CdSe by Somorjai<sup>(49)</sup>; also Pickert<sup>(50)</sup> has found similar evidence in the case of Ag<sub>2</sub>S.

Our results on HgS (table 8) could also be explained on these lines as well as the considerable discrepancy observed always for the data of Hsiao and Schlechten<sup>(15)</sup>. It is not considered however that the data presented here can be taken as a proof for small values of vaporization coefficients.

In general many artefacts can lead to disagreeing vapor pressure data and only careful direct measurements should be taken as proof for a low vaporization coefficient.

6. From heats of formation, heats of atomization (table 11) are calculated. It is interesting to compare here the isosteric groups IV-VI: III-V: II-VI and I-VII. It is obvious from fig.8 that the heat of atomization decreases as the elements forming the compound get further apart from the center (group IV) of the isosteric series. Except for [ZnS] and [CdS] the II<sub>b</sub>-VI<sub>b</sub> compounds form a minimum. Au, Cu and Ag present the same sequence as the heats of vaporization of the elements and dissociation energies of diatomic molecules<sup>(21)</sup> and not the sequence of the periodic table: Cu, Ag, Au. The group III<sub>b</sub>-V<sub>b</sub> compounds seem to follow mainly the trend of group V<sub>b</sub> elements. The same trend is observed for [CdS]: [ZnSe] or [CdSe]: [ZnTe] but the Hg compounds have lower values.

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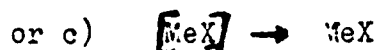
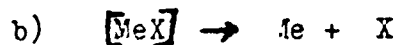
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TABLE I. Relations between evaporated mass, vapor pressure and equilibrium constant of vaporization.



(Examples Pb, HgTe)

$$p_1 = (G_1/st)(2\pi RT/M_1)^{1/2} = K(vap)$$



(Examples ZnS, CdS, HgS, ZnSe, CdSe)

$$p(Me) = (G/st) [2\pi RT/M(Me)]^{1/2} M(Me)/M(MeX)$$

$$p(X_2) = 1/2(G/st) [2\pi RT/M(X_2)]^{1/2} M(X_2)/M(MeX)$$

$$K(vap) = p^2(Me).p(X_2) = 1/2[G/st.M(MeX)]^3(2\pi RT)^{3/2}M(Me).M(X_2)^{1/2}$$



(Examples ZnTe, CdTe)

$$p(Me) = (G/st) [2\pi RT/M(Me)]^{1/2} M(Me)/M(MeX)$$

$$p(X) + 2^{1/2}p(X_2) = (G/st) [2\pi RT/M(X)]^{1/2} M(X)/M(MeX)$$

if  $K' = p^2(X)/p(X_2)$  is known

$K_1(vap) = p^2(Me)p(X_2)$  and  $K_2(vap) = p(Me)p(X)$  is calculated.

TABLE 2. Ion intensity ratios and relative  
ionization cross sections for 70 eV  
electrons.

	$\sigma(X_2)/\sigma(He)$	$\frac{\sigma(X)}{\sigma(He)}$	$\frac{\sigma(X_2)}{\sigma(X)}$
S <sub>2</sub> /Zn	1.15	0.8	1.44
S <sub>2</sub> /Cd	0.83	0.58	1.42
S <sub>2</sub> /Hg	0.68	0.47	1.45
Se <sub>2</sub> /Cd	1.38	0.84	1.64

TABLE 3. Ion intensities in vapor above HgSe at 484°K  
 Electron intensity 30  $\mu$ amp; energy 70 ev. Ion  
 accelerating field 1000 V. Intensities in scale  
 divisions (approx.  $10^{-15}$  amp); sum of isotopic  
 peaks.

Hg <sup>+</sup>	Se <sup>+</sup>	Se <sub>2</sub> <sup>+</sup>	Se <sub>3</sub> <sup>+</sup>	Se <sub>4</sub> <sup>+</sup>	Se <sub>5</sub> <sup>+</sup>	Se <sub>6</sub> <sup>+</sup>	Se <sub>7</sub> <sup>+</sup>	Se <sub>8</sub> <sup>+</sup>
6140	162	800	262	536	660	4200	640	200

TABLE 4. Upper limits of dissociation energies of  
 $\text{II}_b\text{-VI}_b$  molecules.

	$\log I(\text{MX})/I(\text{X}_2)$	T°K	$E(\text{MeX}) <$
ZnS	$<- 4.7$	1270	48
ZnSe	$<- 3$	1000	50
ZnTe	$<- 3.84$	1000	30
CdS	$<- 3$	1000	59 <sup>(*)</sup>
CdSe	$<- 3$	1000	46
CdTe	$<- 3$	1000	31
HgS	$<- 3$	500	53 <sup>(*)</sup>
HgSe	$<- 3$	500	39
HgTe	$<- 3$	500	33

The necessary entropy and heat capacity data for eqn.(11) were taken for the elements from ref.26, for solid compounds as given in the next section of this paper; for gaseous  $\text{MeX}$ :  $S_{298}^0 = 53.8 + 0.043 M(\text{MeX}) - 240/M(\text{MeX})$  e.u.<sup>(27)</sup> and  $C_p = 9$  was taken.

(\*) The lower values of limits found recently<sup>(9)</sup> reduce the value for CdS by about 10 and for HgS by about 5 kcal.

TABLE 5. Vaporization of lead.

T°K:	G grx10 <sup>3</sup>	t sec	-log <sub>10</sub> p (a)	-log <sub>10</sub> p (b)	$\Delta \left[ \frac{G^0 - H^0}{T} \right]_{298}$ (c)	$\Delta H^0_{298.15}$ cal/at.g (d)	(e)
913:	2.90	410	5.710	5.727	24.94	46,700:	46,430:
936:	3.70	3540	5.504	5.525	24.88	46,950:	46,670:
951:	5.73	2790	5.205	5.234	24.82	46,870:	46,530:
984:	5.65	1800	4.945	4.982	24.77	46,810:	46,510:
1008:	11.70	1820	4.722	4.752	24.72	46,840:	46,540:
1032:	13.24	1800	4.474	4.500	24.67	46,710:	46,400:
					$\Delta H^0_{298,15}$	46,810:	46,610:

- (a) Pressures in atmospheres eqn. 2<sup>1</sup> Table 1.  
The effusion area  $s = 1.60 \times 10^{-2}$  cm<sup>2</sup>.
- (b) The same corrected for temperatures rise and fall using the values of col.(a)
- (c) ref.(26).
- (d) Calculated by the third law method (eqn.8) from col.(b) and (c).
- (e) The same assuming a Clausing factor of 0.86 calculated for the thickness of 0.05 cm of the effusion hole and the resistance corresponding to the radiation shields.

TABLE 6. Vaporization of ZnS.

T°K	G(mgr)	t(sec)	log K	s.10 <sup>2</sup> (cm <sup>2</sup> )	ΔH <sub>298</sub> <sup>0</sup>
1044	1.68	3600	-17.539	1.57	190.0
1063	2.86	3600	-16.835	"	189.8
1077	3.75	3800	-16.541	"	190.7
1090	5.48	3600	-15.971	"	190.0
1099	7.06	3600	-15.651	"	189.0
1117	5.56	1800	-15.009	"	189.5
1128	6.38	1800	-14.847	"	190.5
1146	10.77	1800	-14.155	"	189.7
1164	2.00	1810	-13.903	0.241	191.2
1180	3.29	1800	-13.251	"	190.2
1199	4.56	1920	-12.861	"	191.1
1216	6.32	1800	-12.371	"	190.6
1233	8.92	1800	-11.911	"	190.5

The third law value calculated using  $S_{298}^0[\text{ZnS}] = 13.8 \pm 0.2$  e.u and  $C_p(\text{sph}) = 12.16 + 1.24 \times 10^{-3}T - 1.36 \times 10^{-5}T^2$  (27,39). Sphalerite is transformed to wurtzite at 1293°K ( $I_t = 3.2$  kcal)<sup>(27)</sup> we have assumed however that our samples were wurtzite based on an observation of McCabe<sup>(12)</sup> and having degassed our samples in vacuum at high temperature. Assuming that our samples are sphalerite would lead to  $\Delta H_{298}^0 = 189.3$  Kcal.

TABLE 7. Vaporization of CdS

$T^{\circ}\text{K}$	$G(\text{mgr})$	$t_{\text{sec}}$	$\log K$	$s \cdot 10^2 (\text{cm}^2)$	$\Delta H_{298}$
902	3.32	3600	-17.244	1.57	160.3
921	2.87	1320	-16.624	"	160.9
940	4.85	1800	-15.834	"	160.8
941	6.20	1790	-15.504	"	159.5
950	9.13	1390	-15.126	"	160.9
979	17.05	1800	-14.182	"	159.9
988	2.94	1300	-14.058	0.241	160.5
1008	6.15	2040	-13.282	"	160.5
1025	8.00	1890	-12.764	"	160.3
1025	7.50	1800	-12.736	"	160.5
1052	25.45	1640	-11.442	"	159.5
					160.4

Free energy function estimated by Freeman<sup>(29)</sup>.



TABLE 8. Vaporization of  $\text{HgS}$ .

$T^{\circ}\text{K}$	$G(\text{mgr})$	$t(\text{sec})$	$\log K$	$s \cdot 10^2 (\text{cm}^2)$	$\Delta F_{298}^{\circ}$
481	1.34	3260	-18.857	1.57	88.26
490	2.01	3250	-18.314	"	89.28
499	4.58	3150	-17.192	"	88.26
511	9.07	3620	-15.460	"	88.67
523	18.56	3250	-15.372	"	88.04
534	3.95	2760	-14.215	0.107	87.07
544	4.72	3510	-13.574	"	87.24
551	8.54	3010	-12.703	"	86.03
569	15.01	2780	-11.845	"	85.49
					<hr/> 87.7

Free energy function estimated by Freeman<sup>(29)</sup>.

TABLE 3. Standard heats of formation of  
Zn, Cd and Hg sulfides at 298.15°K

[Ref]		$-\Delta H_f^{\circ}, 298 [kcal]$	
(1) This paper	I	48.5	Knudsen 3rd law
		47.9	Knudsen 2nd law
	II	50.4	Mass spectr 3rd law
		48.1	Mass spectr 2nd law
(2) Veselovskii <sup>(15)</sup>		49.1(49.8)*	Knudsen 2nd+3rd law
(3) Fogorelyi <sup>(10)</sup>		48.1(48.4)*	Knudsen (excluding 2 results)
(4) McCabe <sup>(12)</sup>		47.7(47.9)*	Knudsen
(5) Richards <sup>(13)</sup>	I	49.1	transport ZnS+H <sub>2</sub>
	II	49.4(49.3)*	transport ZnS by N <sub>2</sub>
	III	48.8	transport ZnS by N <sub>2</sub> +S <sub>2</sub>
(6) Spandau <sup>(17)</sup>		48.7(49.3)*	transport
(7) Curlook and Fidgeon <sup>(30)</sup>		47.0	ZnS + H <sub>2</sub>
(8) Kapustinski and Vorshunov <sup>(31)</sup>		48.3	calorimetric
(9) Makolkin <sup>(32)</sup>		47.9	electromotive force
(10) Rossini et al. <sup>(33)</sup>		48.5	
		48.5	unweighted mean

TABLE 9. Continued

**[CdS]**

(1) This paper	38.0	Knudsen 3rd law
	39.6	Knudsen 2nd law
(2) Veselovskii <sup>(15)</sup>	37.8	Knudsen*
(3) Fogorelyi <sup>(10)</sup>	37.5	Knudsen*
(4) Spandau <sup>(17)</sup>	37.7	transport*
(5) Malkolkin <sup>(32)</sup>	34.0	E.M.F.
(6) Kapustinski and Vorshunov <sup>(31)</sup>	34.8	calorimetry
(7) Rossini et al. <sup>(33)</sup>	34.5	
	<u>38.0</u>	proposed value

**[H<sub>2</sub>S] red**

(1) This paper	13.8	Knudsen 3rd law
(2) Rinse <sup>(34)</sup>	14.0	Manometric
(3) Treadwell <sup>(35)</sup>	14.0	Transport and H <sub>2</sub> /H <sub>2</sub> S equilibrium
(4) Goates et al. <sup>(36)</sup>	11.2	E.M.F.
(5) Rossini et al. <sup>(33)</sup>	13.9	from older data including (35,37)
(6) Freeman <sup>(29)</sup>	<u>12.7</u>	
	13.8	proposed value

\* calculated by Freeman<sup>(29)</sup>

TABLE 10. Thermodynamic data on selenides and tellurides of  
Zn, Cd and Hg.

[ZnSe]	$-\Delta H_{298}^{\circ}$	$S_{298}^{\circ}$ [MeX]	
(1) This paper	39.3	19.8	Knudsen 2nd law
(2) Korneeva <sup>(42)</sup>	52.	7	Knudsen recal 2nd law
	37.2	20.	3rd law
(3) Rossini <sup>(33)</sup>	34.		
(4) Wösten and Gers	$\frac{47}{39}$	$\frac{14.6}{20}$	transport 2nd law proposed value
<hr/>			
[CdSe]			
(1) This paper	32.5	23.1	Knudsen 2nd law
(2) Korneeva <sup>(42)</sup>	33.2	21.	Knudsen recal 2nd law
(3) Somorjai <sup>(43)</sup>	25.0	20.9	total pressure
(4) Wösten <sup>(44)</sup>	37.5	18.4	transport
	$\frac{32.5}{32.5}$	$\frac{23.1}{23.}$	proposed value
<hr/>			
[HgSe]			
(1) This paper	14.0		Mass spectro- metric $\text{Se}_6/\text{Se}_2$ equilibrium
(2) Rossini <sup>(33)</sup>	5.		calorimetric

TABLE 10. Continued

**[ZnTe]**

(1) This paper	24.9	23	Knudsen 2nd law
(2) our data combined with McAteer and Seltz <sup>(45)</sup>	25.1	22.0	E.W.F.
(3) Korneeva <sup>(42)</sup>	24.3	22.	
(4) Rossini <sup>(33)</sup>	30.	10.	see also ref.33
	26.	22.	proposed value

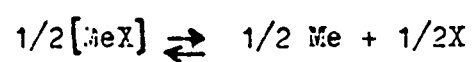
**[CdTe]**

(1) our data	23.8	24.	Knudsen
(2) McAteer and Seltz <sup>(45)</sup>	24.3	22.6	E.W.F., see also ref.33.
(3) Korneeva <sup>(42)</sup>	22.3	25.6	Knudsen 2nd law
(4) Lorentz <sup>(46)</sup>	24.8	20.	pressure 2nd law
	24.	23.	proposed value

**[HgTe]**

12.	22.	Knudsen 2nd law
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TABLE 11. Heats of atomization in kcal/atom gr.



	S	Se	Te
Zn	73	63	52
Cd	66	57	48
Hg	47	42	37

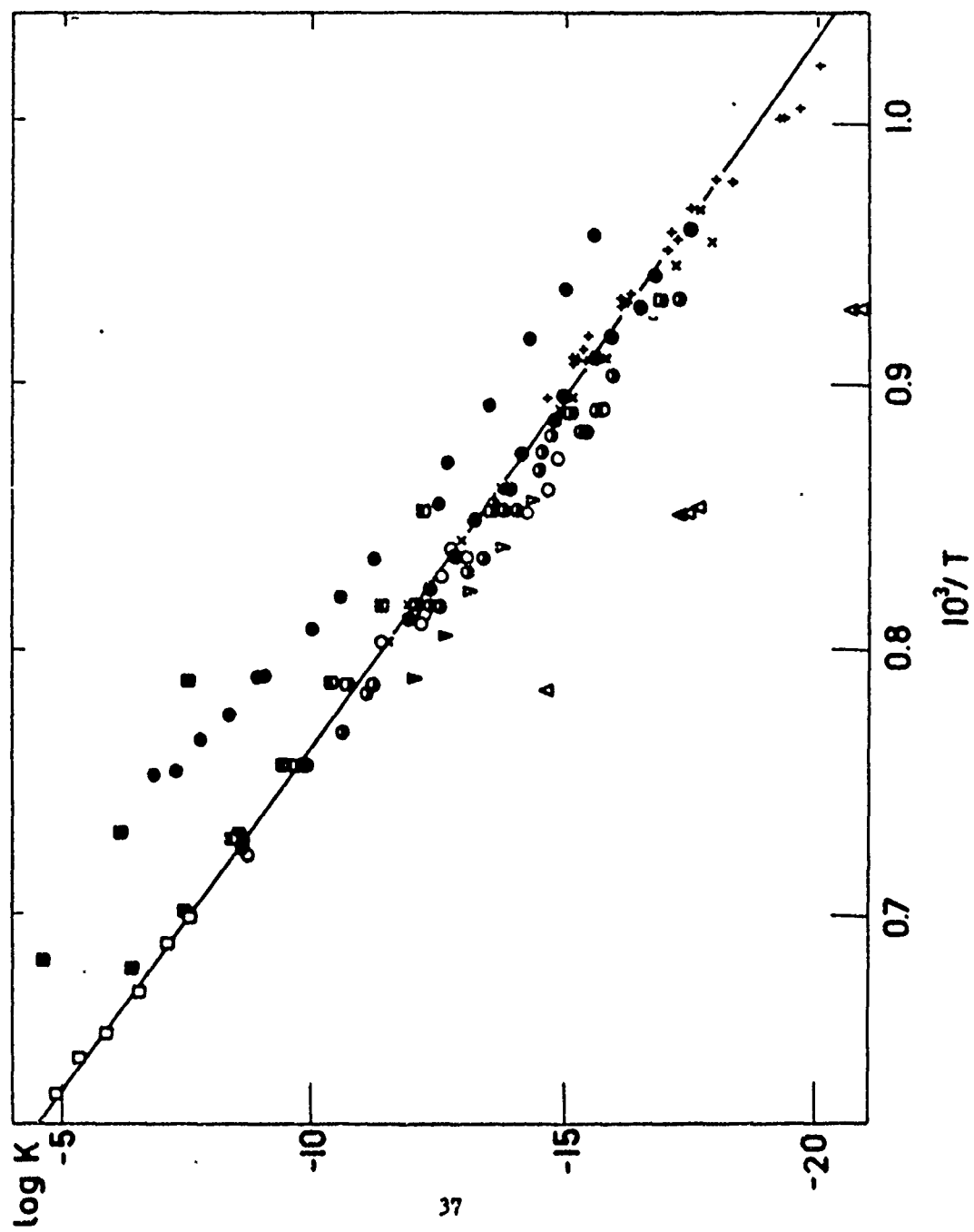


Figure 1 Vaporization of  $[ZnS]$

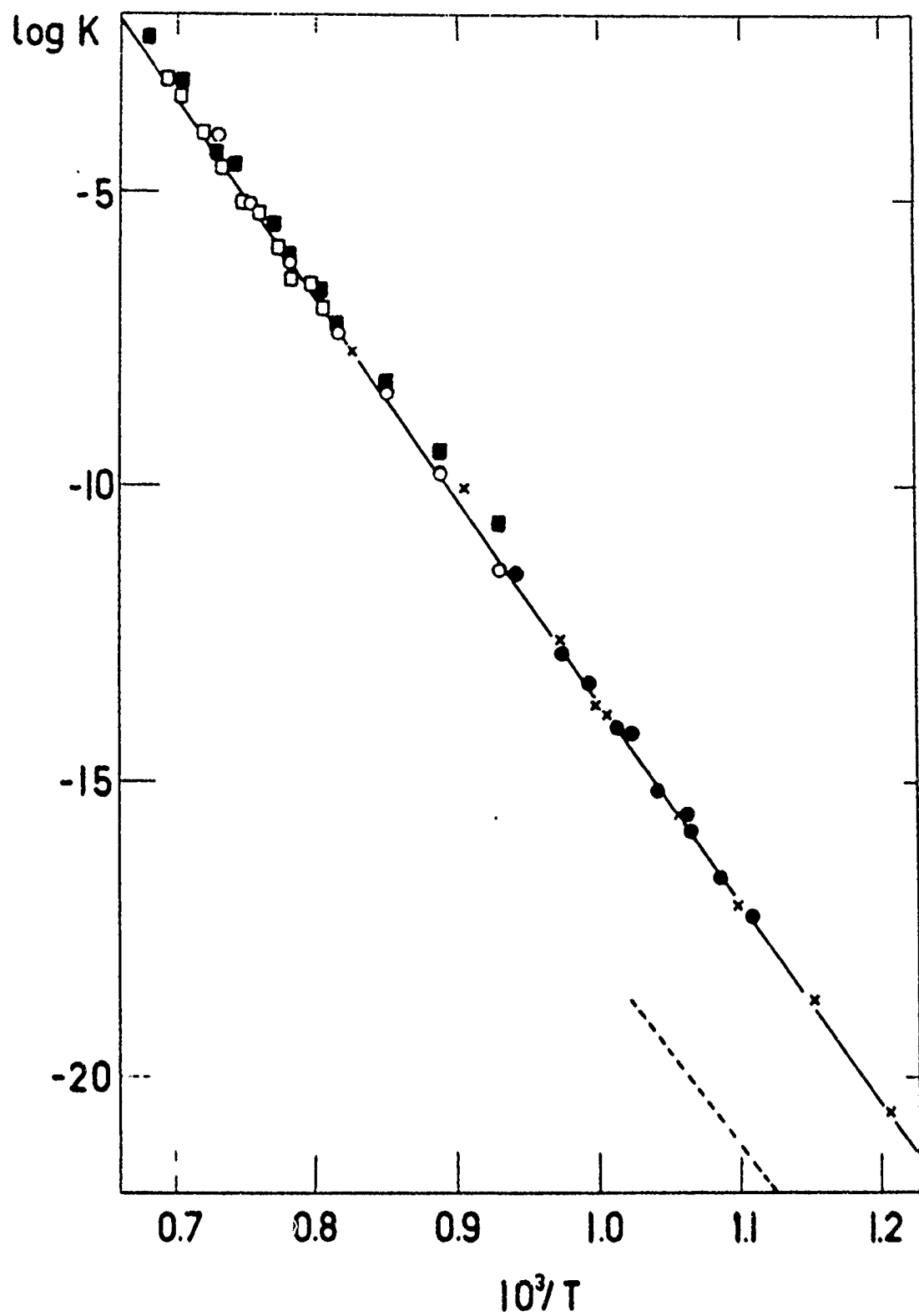


Figure 2 Vaporisation [45]



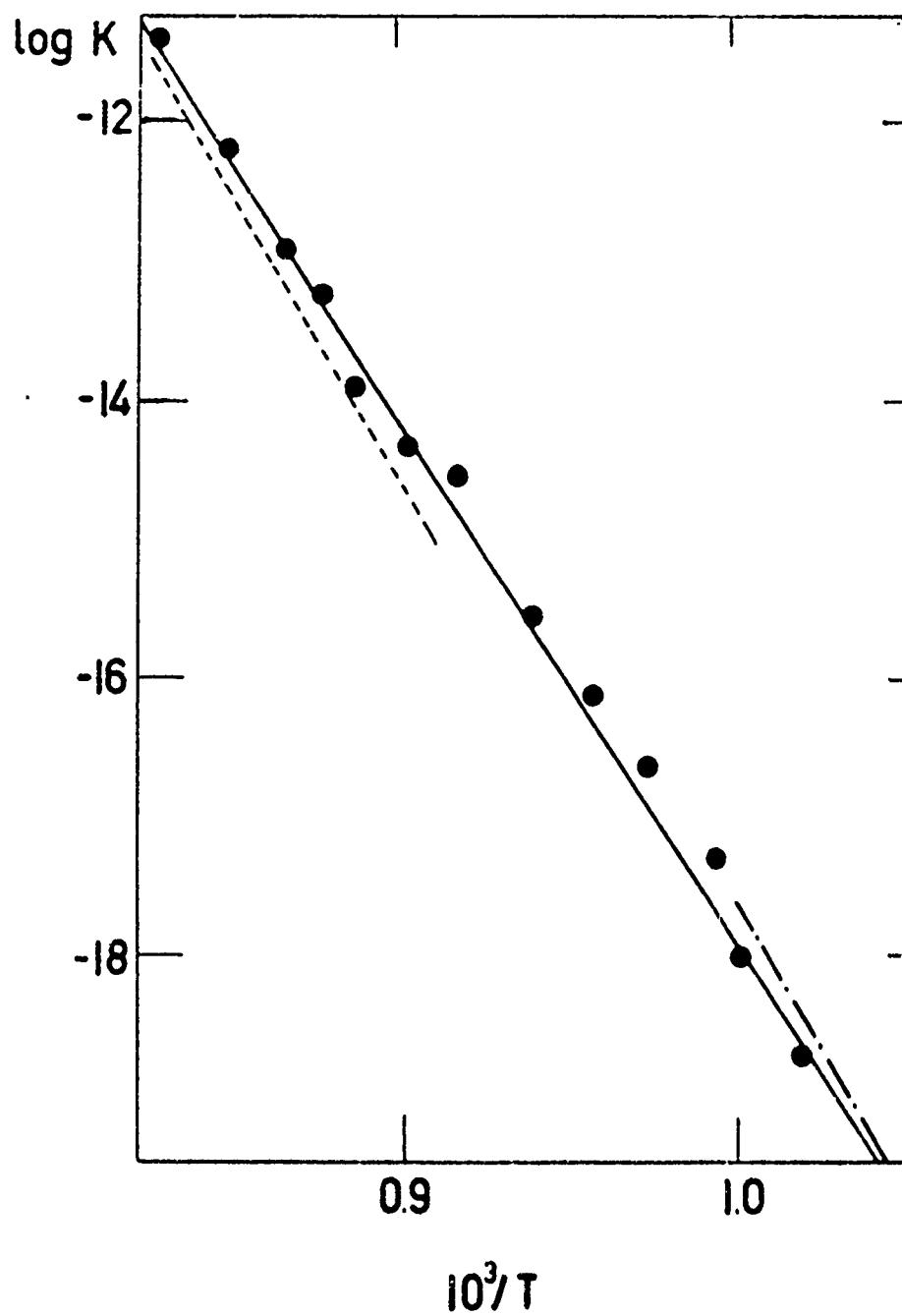


Figure 3 Vaporisation of  $[ZnSe]$

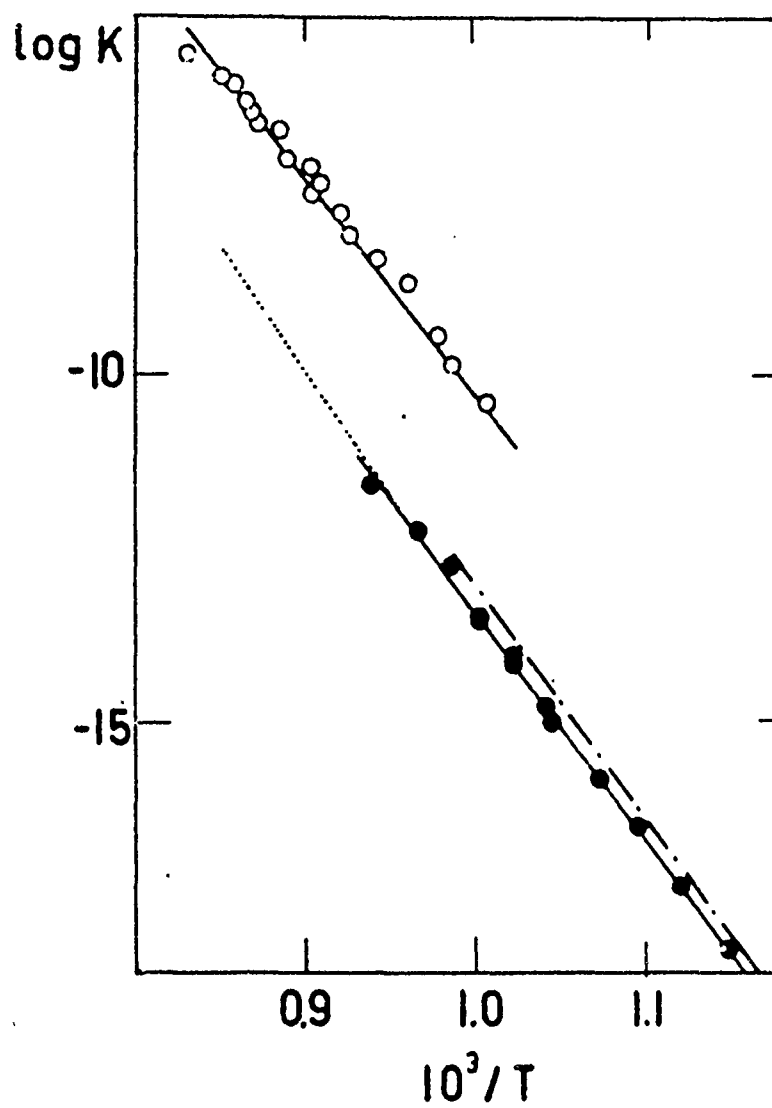


Figure 4 Vaporization of  $[\text{CdSe}]$

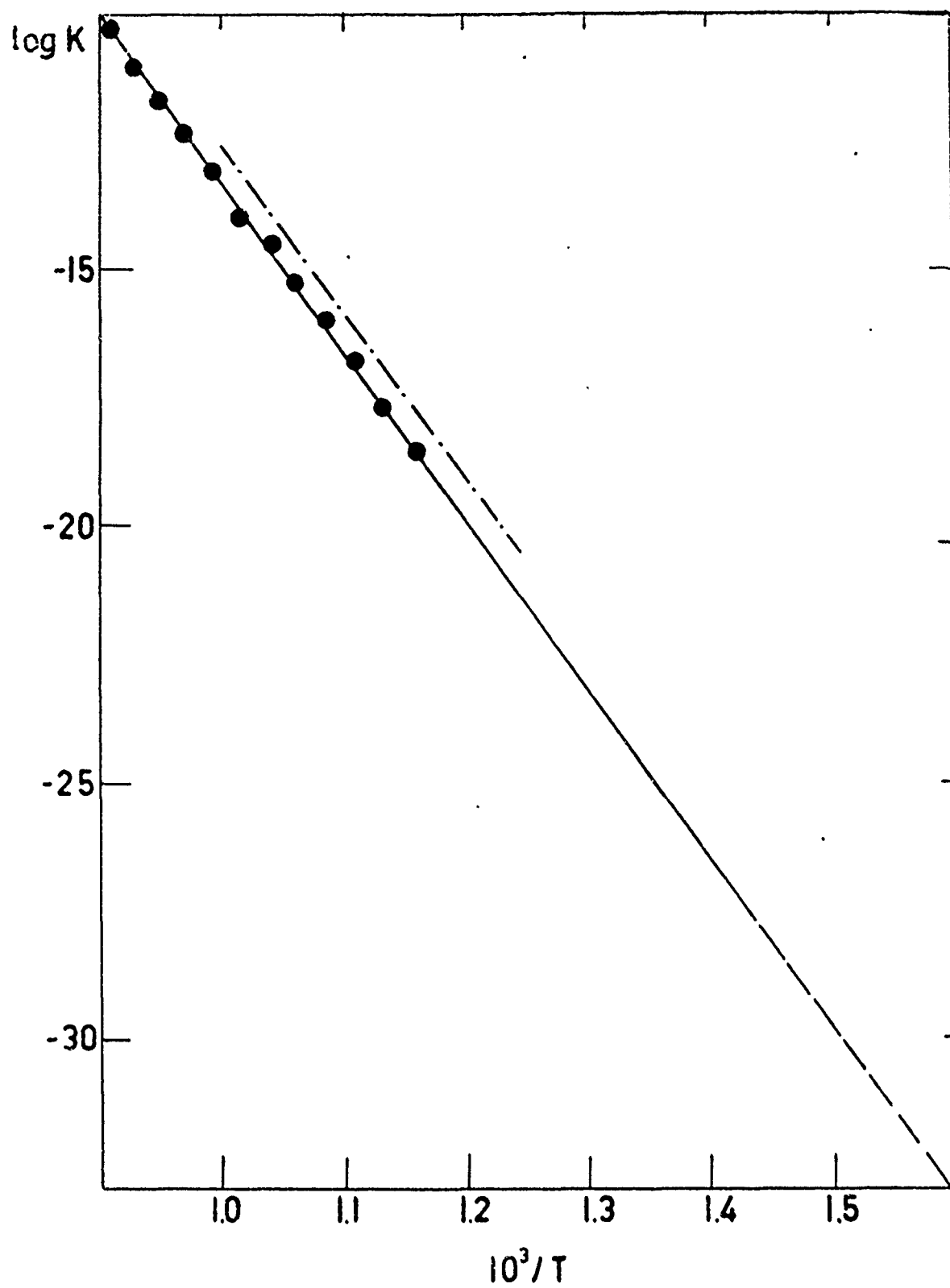


Figure 5 Vaporization of  $\text{ZnTe}$

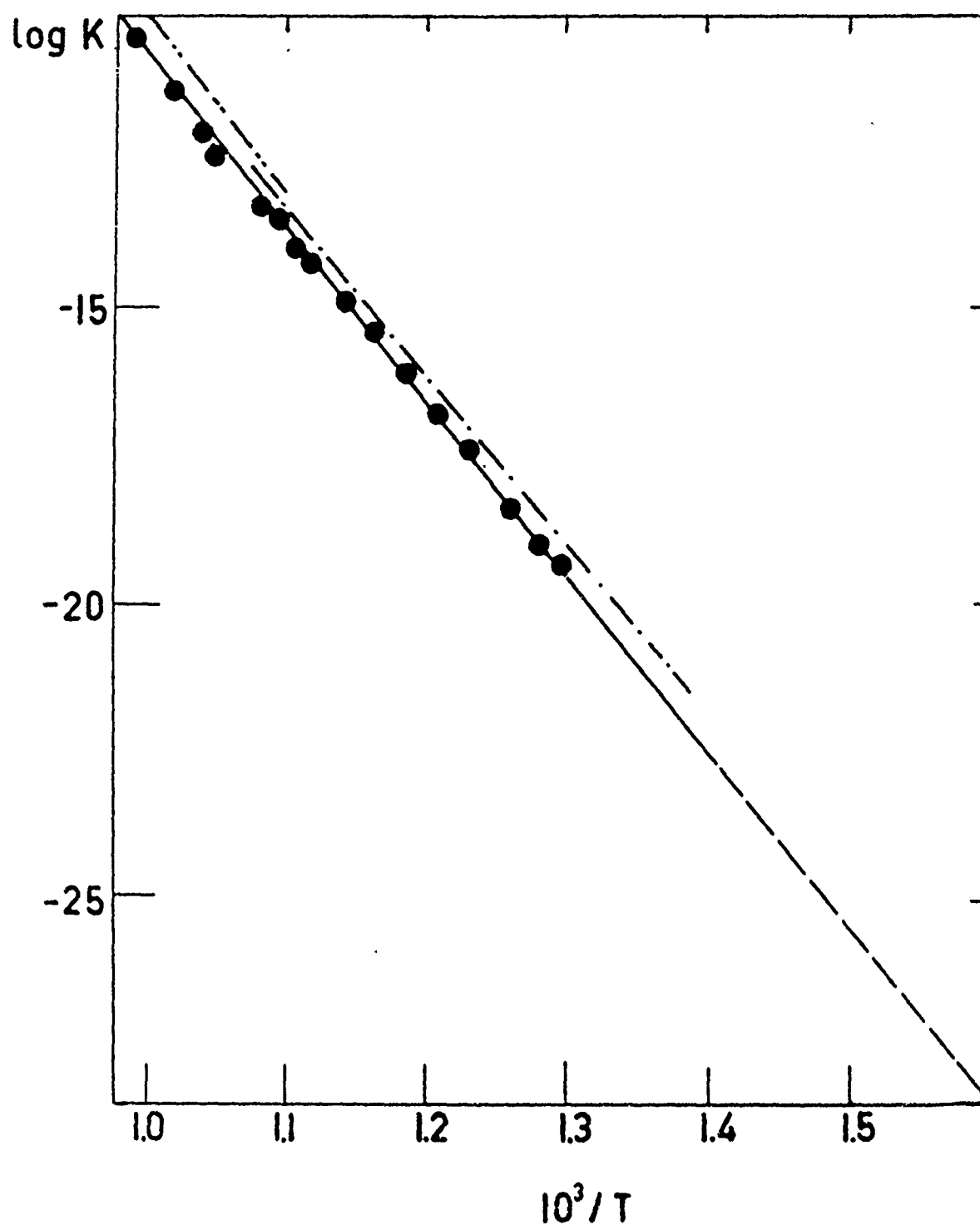


Figure 6 Vaporisation of  $\text{CdTe}$

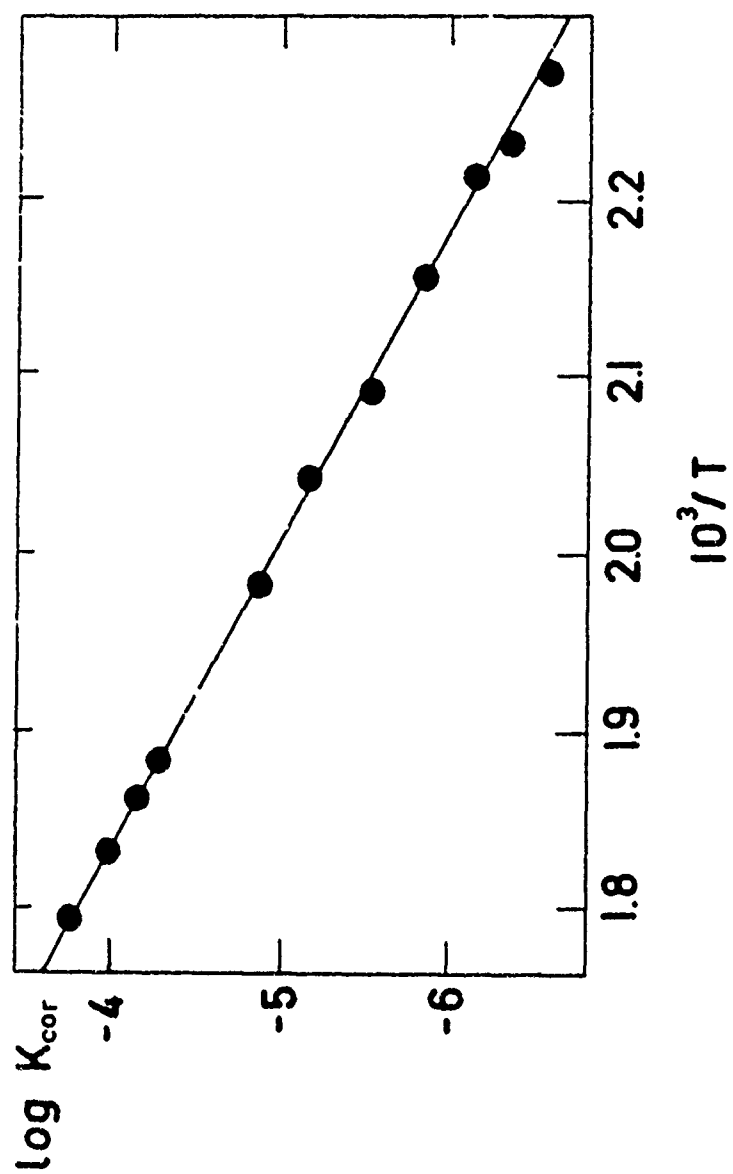


Figure 7 Vaporization of  $\text{HgTe}$

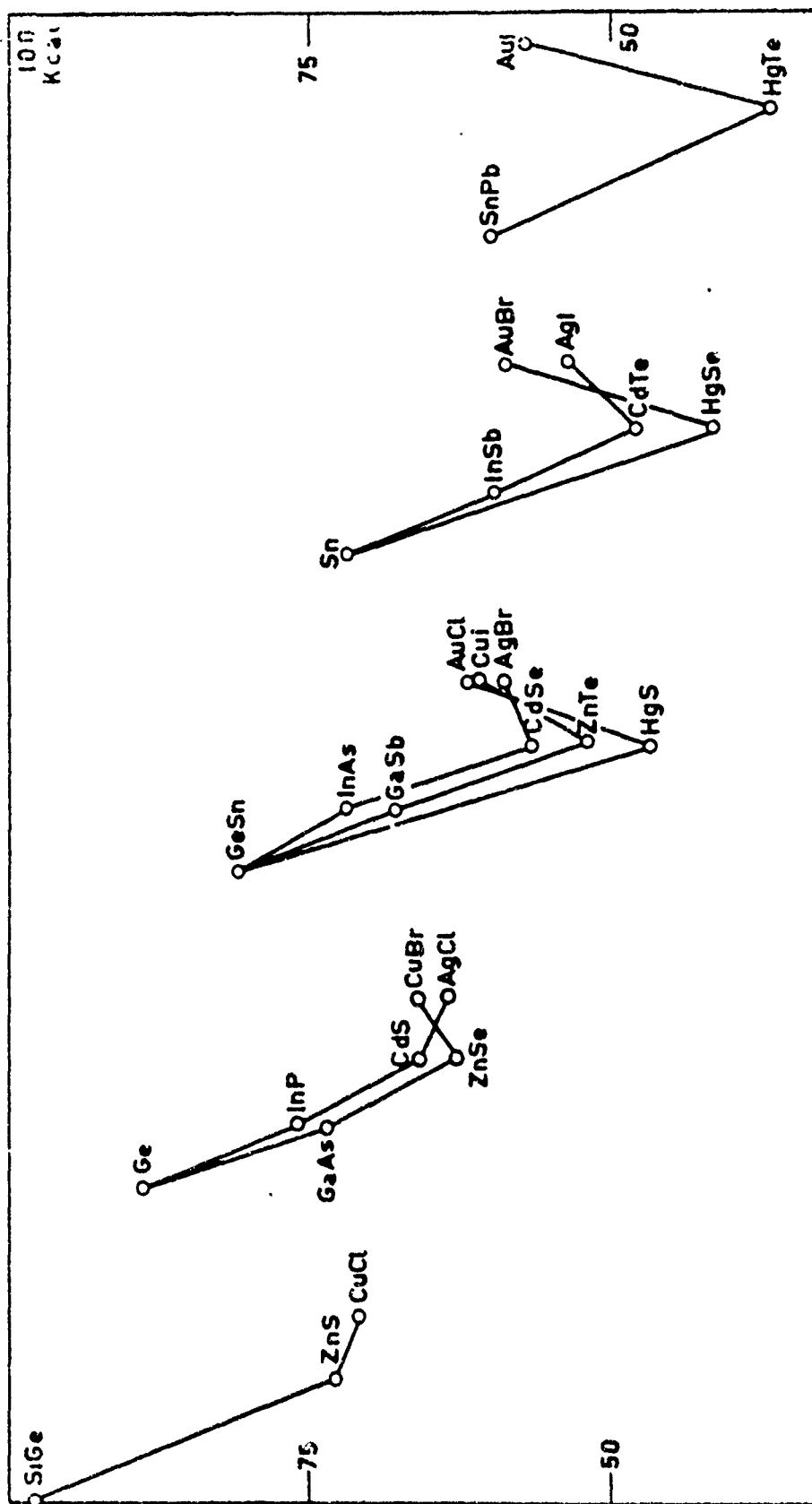


Figure 8 Heats of Atomization in kcal per gram Atom for Isosteric Compounds